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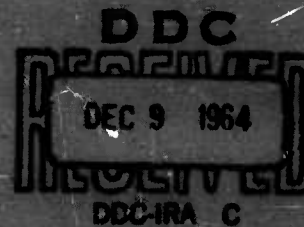
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Nonequilibrium Rocket Nozzle Recombination Losses

15 OCTOBER 1964

Prepared by E. A. COOK and L. SCHIELER
Aerodynamics and Propulsion Research Laboratory

Prepared for BALLISTIC SYSTEMS AND SPACE SYSTEMS DIVISIONS

AIR FORCE SYSTEMS COMMAND

LOS ANGELES AIR FORCE STATION

Los Angeles, California

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CONTRACT NO. AF 04(695)-469

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E. A. Cook and L. Schieler
Aerodynamics and Propulsion Research Laboratory

Laboratory Operations
AEROSPACE CORPORATION
El Segundo, California

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Prepared

E. A. Cook
E. A. Cook

Approved

J. G. Logan
J. G. Logan, Director
Aerodynamics and Propulsion
Research Laboratory

L. Schieler
L. Schieler, Head
Chemical Propulsion
Department

This technical documentary report has been reviewed and is approved for publication and dissemination.   The conclusions and findings contained herein do not necessarily represent an official Air Force position.

For Space Systems Division
Air Force Systems Command

John T. Allton
John T. Allton
Captain, USAF

ABSTRACT

Nonequilibrium performance losses are interpreted in terms of radical concentrations and extent of recombination throughout the expansion process. A brief description of the Bray method for determining the location of departure from equilibrium flow in a rocket nozzle is given. The analysis is applied to N_2O_4-aerozine, H_2-O_2 and H_2-F_2 propellants and a hypothetical H_2-Cl_2 system to obtain the point of effective freezing as a function of area ratio. The kinetic rates for the reactions occurring in the combustion process are discussed, and the values for the rates are included.

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FIGURES

TABLES

NOMENCLATURE

A, B   concentrations of reactants, moles gm^{-1}

C*   characteristic velocity, ft sec^{-1}

g   gravity, 32.17 ft sec^{-1}

k_b backward rate constant, $\begin{cases} cc \ mole^{-1} \ sec^{-1} \text{ for bimolecular reactions} \\ cc^2 \ mole^{-2} \ sec^{-1} \text{ for three-body reactions} \end{cases}$

k_f forward rate constant

I_s specific impulse

M   average gas molecular weight, g $mole^{-1}$

MR   mixture ratio, weight of oxidizer/weight of fuel

N   number of moles per reaction, moles g^{-1}

P_c chamber pressure, lb in^{-2}

r_k kinetic rate of recombination

r_s recombination rate required for equilibrium

r_t throat radius, in.

R   gas constant, 1.987 cal

RC   rate controlling

T   temperature, °K

T_f temperature at freeze point, °K

x   distance, ft

NOMENCLATURE (Continued)

β nozzle half angle

ϵ area ratio

ϵ_f area ratio of freezing

μ velocity, ft sec^{-1}

ρ density, gm cc^{-1}

I. INTRODUCTION

At the high temperatures usually encountered in the combustion of rocket propellants, the product gases are composed of stable molecules, partially dissociated molecules, and free radicals. The calculation of theoretical propellant performance and gas composition by means of shifting equilibrium methods is based on the assumption of infinitely rapid rates of reaction in the combustion chamber and during the nozzle expansion process. Maximum propellant performance is predicted, since at any pressure and temperature the enthalpy release corresponding to maximum recombination is achieved.

Frozen propellant performance is based on the assumption of zero reaction rates starting at some point in the rocket motor. The classic freeze point in the older literature was the chamber gas composition. From the chamber throughout the nozzle expansion the gas composition remained the same. More recent approximate methods of calculation show that in actual engines the freeze point should be in the vicinity of the throat. The exact area ratio where freezing takes place varies with the motor and propellant so each case must be interpreted individually to determine the performance for the system.

A comparison of performance achieved from equilibrium flow throughout the nozzle and from freezing at different points is shown in Table 1 for several typical propellants.

If the composition of the combustion products of various propellants is frozen at the throat or not permitted to change as a function of the expansion process, the effect on performance varies with the chemical composition and the mixture ratio of the propellant (Table 1). For example, the $Al-H_2-O_2$ propellant suffers almost no loss in performance when it is frozen at the throat, while $OF_2-B_2H_6$ shows a considerable loss. This difference is obvious when the composition (Table 2) at the throat is examined. The number of moles of atoms and radicals available for recombination

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Table 1. Comparison of Frozen and Equilibrium Specific Impulses

Propellant	MR	Moles of Free Atoms or Radicals	Shifting I_s $\epsilon = 10$	Shifting I_s $\epsilon = 50$	I_s Loss, % $\epsilon = 10$ $\epsilon_f = 1.0$	I_s Loss, % $\epsilon = 50$ $\epsilon_f = 1.0$	I_s Loss, % $\epsilon = 10$ ϵ_f = chamber	I_s Loss, % $\epsilon = 50$ ϵ_f = chamber	I_s Loss, % $\epsilon = 10$ $\epsilon_f = 2.0$	I_s Loss, % $\epsilon = 50$ $\epsilon_f = 2.0$
$OF_2 - B_2H_6$	4.0	1.28	404.7	448.8	5.7	8.3	--	--	--	--
$F_2 - N_2H_4$	2.3	0.7874	396.3	430.5	6.1	8.5	--	--	--	--
$Al-H_2-O_2$	20% Al MR = 2.0	0.007	425.8	455.0	0.03	0.02	--	--	--	--
$Be-H_2-O_2$	25% Be MR = 1.91	0.169	496.6	539.8	1.1	1.4	--	--	--	--
O_2-H_2	3.1	0.014	422.9	451.6	0.14	0.10	--	--	--	--
	4.5	0.166	425.6	456.2	0.83	1.11	--	--	--	--
	6.33	0.554	415.1	460.3	3.1	4.3	--	--	--	--
F_2-H_2	4.0	0.041	436.0	460.6	0.89	1.00	0.31	0.37	0	0
	7.0	0.483	446.3	476.0	2.6	3.4	4.36	5.31	0.15	.36
	11.0	1.00	444.7	480.6	4.8	6.9	7.04	9.33	1.2	2.4

Table 2. Gas Compositions, $P_c = 1000$ lb in^{-2}

Combustion Products Moles/100 g	OF_2-B_2H_6 MR = 4.0		Combustion Products Moles/100 g	F_2-N_2H_4 MR = 2.3	
	Chamber	Throat		Chamber	Throat
H	1.03752	0.97877	H	0.41974	0.34679
B	0.00055	0.00031	N	0.00403	0.00237
O	0.12013	0.09378	F	0.54595	0.43794
F	0.12069	0.09081	NH	0.00060	0.00032
BH	0.00002	0.00001	HF	3.2237	3.23044
HBO_2	0.03885	0.04168	H_2	0.11953	0.10213
OH	0.13316	0.11301	NH_2	0.00003	0.00001
HF	1.54425	1.56241	N_2	0.94313	0.94411
H_2	0.67466	0.70094	F_2	0.00005	0.00002
H_2O	0.11543	0.11813	H, A, F, NH	0.9703	0.7874
BO	0.11552	0.09991			
BOF	0.90003	0.95770	H_2/O_2 MR = 3.1		
BF	0.38122	0.33753			
BF_2	0.00103	0.00078			
BF_3	0.00490	0.00432	H	0.03350	0.01261
B_2O_2	0.00083	0.00073	O	0.00001	0.00000
B_2O_3	0.00044	0.00048	OH	0.00414	0.00109
O_2	0.00826	0.00635	H_2	7.35794	7.36683
H, B, O, F, OH	1.412	1.277	H_2O	4.72146	4.72453
			O_2	0.00000	0.00000
H_2-F_2 MR = 4.0			H, O, OH	0.03765	0.01370
H	0.11172	0.04129	H_2-O_2 MR = 4.5		
F	0.00034	0.00006			
HF	4.21019	4.21047			
H_2	7.75972	7.79476	H	0.18527	0.11961
H, F	0.11206	0.04135	O	0.00270	0.00096
			OH	0.08432	0.04506
			H_2	3.85918	3.86883
H_2-F_2 MR = 7.0			H_2O	5.02405	5.06669
			O_2	0.00143	0.00052
			H, O, OH	0.27229	0.1656
H	0.68524	0.47401			
F	0.01881	0.00868			
HF	4.58645	4.59658			
H_2	3.56458	3.66586			
H, F	0.70405	0.48269			

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Table 2. Gas Compositions, P_c = 1000 lb in^{-2} (Continued)

Combustion Products Moles/100 g	H_2-F_2 MR = 11.0		Combustion Products Moles/100 g	H_2-O_2 MR = 6.33	
	Chamber	Throat		Chamber	Throat
H	1.08504	0.90394	H	0.27057	0.22593
F	0.15996	0.09785	O	0.04155	0.02903
HF	4.66476	4.72689	OH	0.37867	0.29929
H_2	1.25705	1.31656	H_2	1.57128	1.51476
H, F	1.24500	1.00179	H_2O	4.87270	4.99120
			O_2	0.05212	0.03882
	Al-H_2-O_2 Al-20% O_2/H_2 = 2.0		H, O, OH	0.69079	0.5542
H	0.01735	0.00654			
H_2O	2.22129	2.22168			
H_2	10.99398	10.99919			
Al_2O_3(c)	0.37064	0.37064			
OH	0.00052	0.00014			
H, OH	0.01787	0.00668			
	Be-H_2-O_2 Be-25% O_2/H_2 = 1.91				
H	0.16324	0.16715			
Be	0.00112	0.00110			
O	0.00001	0.00001			
BeH	0.00025	0.00018			
BeOH	0.03730	0.03720			
OH	0.00076	0.00072			
H_2	12.38739	12.38558			
Be(OH)$_2$	0.00013	0.00012			
H_2O	0.21012	0.21008			
BeO	0.00001	0.00001			
Be_2O_2	0.00004	0.00004			
Be_3O_3	0.00060	0.00082			
Be_4O_4	0.00000	0.00001			
Be_6O_6	0.00000	0.00001			
BeO(c)	2.79961	2.79909			
H, Be, O, OH	0.16513	0.16898			

varies for the propellant and mixture ratio. In the $Al-H_2-O_2$ propellant there are only 0.007 moles of H and OH which would combine to form H_2O and therefore release additional heat if the system were permitted to proceed to complete the recombination. The loss in energy by restricting the recombination is small and therefore causes only small losses in performance. In the $OF_2-B_2H_6$ propellant there are 1.28 moles of H, B, O, F, and OH which are not permitted to recombine, causing larger energy and performance losses. Performance losses are proportional to the energy losses caused by the freezing process.

A comparison of performance degradation among the various mixture ratios of H_2-O_2 reveals the same relationship. At a mixture ratio of 3.1, only 0.014 atoms are restricted from recombining, while at 6.3, 0.554 moles remain as free atoms or radicals after the freezing process.

Available specific impulse is determined by

$$I_s = \left[\frac{2J}{g} (H_c - H_e) \right]^{1/2} \tag{1}$$

where I_s is specific impulse, g is the gravitational constant, J is the mechanical equivalent of heat, H_c is the chamber enthalpy, and H_e is the exhaust enthalpy. In order to obtain maximum specific impulse it is thus necessary to maximize H_c and minimize H_e. The value of H_c is fixed by the propellant combination, but H_e is a function of the nozzle expansion ratio, the kinetics, and the enthalpies of the chemical reactions which occur during expansion. The combination of Eq. (1) with its derivative (Ref. 1) with respect to H_e leads to Eq. (2):

$$\frac{dI_s}{I_s} = \frac{dH_e}{2(H_e - H_c)} \tag{2}$$

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which shows that the fractional loss in specific impulse is proportional to the H_e loss due to unrecombined free radicals. In many chemical rockets this specific impulse loss can be as high as 10 per cent.

In actual nozzles, the residence time of the combustion gases is of the order of a few milliseconds, and the idealized conditions of shifting thermodynamic equilibrium may not be achieved. For actual nozzles, some recombination reactions usually occur, and the achievable performance will lie between the shifting and frozen equilibrium values. The magnitude of the nozzle recombination performance loss will depend on factors such as P_c, P_o, ϵ, and nozzle geometry which determine velocity and residence time of the combustion gases.

Because of the complexity of a complete kinetic analysis of nonequilibrium flow in nozzles and lack of accurate kinetic rate constants, considerable interest has been directed toward approximate methods of calculation. Bray (Ref. 2) in 1959 proposed that nozzle recombination losses could be approximated by assuming equilibrium flow to a selected point in the nozzle followed by frozen flow for the remainder of the nozzle expansion process. In a recombination reaction the principal mechanism governing recombination is a three-body reaction, $A + B + M \rightarrow AB + M$, in which A and B are identical or dissimilar free radicals, and M is any third body. The energy liberated in three-body recombination reactions is usually at least an order of magnitude greater than binary exchange reactions of the type $A + B \rightarrow C + D$. Bray showed that although there are many possible three-body recombination reactions the number of freeze points[1] is equal to the number of free radicals less the number of independent binary exchange reactions. Reduction of the number of freeze points occurs because of the rapid binary exchange reactions which couple the free radical and recombination reactions. Since the Bray approximation method is not a routine calculation but varies with gas composition, the methodology is best illustrated by the examples which follow.

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[1] These are the points in the rocket nozzle at which equilibrium gas composition cannot be maintained and beyond which a frozen gas composition is expanded isentropically.

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II.   NOZZLE PARAMETERS FOR BRAY ANALYSIS

At the freeze point the kinetic rate and the recombination rate required
by the nozzle must be of the same order of magnitude to be consistent with
the concept of the rapid transition from equilibrium to frozen composition.
Bray's detailed comparison showed that the ratio of the above two rates at
the freeze point was close to unity (Ref 2).   Thus, he assumed that the freeze
point could be approximated by equating the kinetic rate, r_k, to that required
by the nozzle, r_s.

The reaction rate required to maintain shifting equilibrium in the
nozzle is given by Eq. (3):

$$r_s = \frac{2gP_c \tan \beta}{C^* r_t \sqrt{\epsilon}}\left(\frac{dN}{d\epsilon}\right) = \frac{1780.7 P_c}{C^* r_t}\left(\frac{\tan \beta}{\sqrt{\epsilon}}\right)\left(\frac{dN}{d\epsilon}\right) \tag{3}$$

For the derivation of Eq. (3) it is assumed that the reaction rate
required to maintain shifting equilibrium in the nozzle may be defined by
the following equation

$$r_s = \rho \frac{dN}{dt} = \rho\mu\left(\frac{d\epsilon}{dx}\right)\left(\frac{dN}{d\epsilon}\right)$$

where ρ is density, μ is gas velocity, and x is linear nozzle distance.   From
geometrical considerations it can be shown that

$$\frac{d\epsilon}{dx} = \frac{2\sqrt{\epsilon} \tan \beta}{r_t}$$

and from the theory of rocket propulsion that

$$\rho\mu = \frac{gP_c}{\epsilon C^*}$$

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In the preceding equations β is the nozzle half angle, r_t is the nozzle throat radius, g is the gravitational constant, P_c is chamber pressure, and $C*$ is the characteristic velocity. Substitution of the relationships for $d\epsilon/dx$ and $\rho\mu$ into the equation for r_s leads to Eq. (3).

Solution of Eq. (3) requires evaluation of $dN/d\epsilon$ from the shifting equilibrium nozzle compositions and $\tan\beta/\sqrt{\epsilon}$ by measuring the slope at various ϵ stations in the nozzle. For a conical nozzle β is constant, except for the curved section near the throat. Substitution of concentrations of the reactants at various values of ϵ permits the calculation of r_k, the kinetic rate of combination. For a three-body reaction $r_k = k_f ABM$ when concentrations are expressed in moles per cc or $k_f AB\rho^3/M$ when concentrations are expressed in moles per gram, and M is the average molecular weight of the exhaust gases. The third-body concentration is taken to be the total gas composition. The value of ϵ at which $r_s = r_k$ is by definition the freeze point. The value of the kinetic specific impulse is determined by employing shifting equilibrium composition to the freeze point and freezing the gas composition for the remainder of the nozzle expansion process (Ref. 3).

III. HYDROGEN-OXYGEN SYSTEMS

The first step for any Bray analysis is the determination of the important chemical species formed from the combustion process and the pertinent chemical reactions occurring between the species.   When possible, the equations are written in an exothermic direction, and the products of the reactions are those whose concentrations increase during the expansion process.

The changes in equilibrium gas composition which occur as a function of mixture ratio are illustrated in Table 3.   For hydrogen-oxygen systems with mixture ratios as low as 1.6 and 2.4, such small amounts of free radicals are present that recombination reactions are not significant.   The composition is almost frozen in the chamber.

At the higher mixture ratios, there are sufficient free radicals present to influence the energy released from possible recombination reactions.   It now becomes practical to estimate a Bray freeze point by choosing the kinetic steps which apply.   Since OH, H and O are free to form H_2, H_2O and O_2, reactions involving these radicals are considered.   Possible steps might consist of the following (Ref. 4).

Reactions	Rate Constants	ΔH_{298}(kcal mole^{-1})
①[a] $H + OH + M \rightarrow H_2O + M$	$k_1 = 3 \times 10^{19}\ T^{-1}$	-119.2
② $H + H + M \rightarrow H_2 + M$	$k_2 = 2 \times 10^{18}\ T^{-1}$	-104.2
③ $O + O + M \rightarrow O_2 + M$	$k_3 = 2 \times 10^{18}\ T^{-1}$	-119.0
④ $H + O + M \rightarrow OH + M$	$k_4 = 2 \times 10^{18}\ T^{-1}$	-102.3
⑤ $H_2O + H \rightarrow H_2 + OH$	$k_5 = 10^{15}\ e^{\frac{-2.5 \times 10^4\ cal}{RT}}$	15.0
⑥ $O_2 + H \rightarrow OH + O$	$k_6 = 5 \times 10^{14}\ e^{\frac{-1.8 \times 10^4\ cal}{RT}}$	16.7
⑦ $H_2 + O \rightarrow OH + H$	$k_7 = 7 \times 10^{12}\ e^{\frac{-8.5 \times 10^3\ cal}{RT}}$	1.9
⑧ $H_2O + O \rightarrow OH + OH$	$k_8 = 5 \times 10^{14}\ e^{\frac{-1.8 \times 10^4\ cal}{RT}}$	16.9
⑨ $H_2 + O_2 \rightarrow 2OH$	$k_9 = 1 \times 10^{14}\ e^{\frac{-7.0 \times 10^4\ cal}{RT}}$	18.33
[a] ○ corresponds to reactions. In each section the numbering sequence starts over.		

Table 3. Gas Composition for Hydrogen-Oxygen Systems, P_c = 100 lb in^{-2}

Combustion Products (Moles/100 g)	MR = 1.6		MR = 2.4		MR = 3.5		MR = 4.5		MR = 5.2	
	Chamber	Throat	Chamber	Throat	Chamber	Throat	Chamber	Throat	Chamber	Throat
OH	--	--	0.00063	0.00009	0.03391	0.01357	0.14894	0.09123	0.27307	0.19769
H	0.00013	0.00001	0.0142	0.0034	0.18030	0.09373	0.37194	0.26619	0.44538	0.35727
H_2	15.23107	15.23113	10.16977	10.17477	5.98262	6.01464	3.81301	3.82592	2.74569	2.72386
H_2O	3.84625	3.84625	4.41136	4.41178	4.83804	4.85929	4.9443	5.01323	4.89608	4.99965
O	--	--	--	--	0.00073	0.00016	0.0099	0.00446	0.02962	0.01776
O_2	--	--	--	--	0.00025	0.00005	0.00526	0.00241	0.02156	0.01338

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Since there are six species containing two elements, four reactions containing all six species are needed to describe or couple the changes in concentration. Both H_2 and H_2O increase throughout the expansion process, while H, OH, O, and O_2 decrease. Wherever possible it is desirable to write the equation in the direction of increasing H_2 and H_2O to describe the chemical process actually occurring and also to maintain a positive concentration change in the final algebraic expression.

Assuming unit concentrations, the possible reaction can be inspected for their relative rates and for their energy changes. The bimolecular exchange reactions, ⑤ through ⑨, explain the interdependence of the chemical species. They are faster than the three body reactions, ①️ through ④, and therefore are assumed to be more nearly in equilibrium and are not rate-controlling phenomena. The three-body reactions are very exothermic and represent the recombination occurring in the nozzle expansion. Since the three-body reactions release the most energy and are rate controlling, the pertinent ones should be selected. For the hydrogen-oxygen case the water and hydrogen recombination steps should be considered. Both O_2 and OH decrease in concentration with time, so their terminal three-body reactions are discounted. Two other equations from ⑤ through ⑨ should be selected to adequately account for all the species. Reaction ⑨ is not kinetically feasible process because of the high activation energy needed to break the H_2 and O_2 bonds. The remaining reactions have similar rates, assuming unit concentrations, and a choice among them becomes mostly an algebraic one. The four reactions chosen were

② $H + H + M \rightarrow H_2 + M$

① $H + OH + M \rightarrow H_2O + M$

⑥ $O_2 + H \rightarrow OH + O$

⑧ $H_2O + O \rightarrow 2\ OH$

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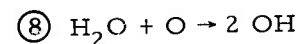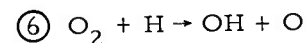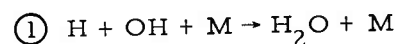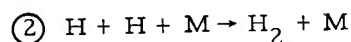
In describing each reaction in terms of the formation or disappearance of one specie the following expressions are obtained:

$$r_8 = -\frac{dH_2O}{d\epsilon} + r_1$$

where

$$r_1 = -\frac{dH}{d\epsilon} - 2r_2 - r_6$$

and where

$$r_2 = \frac{dH_2}{d\epsilon}$$

$$r_6 = -\frac{dO_2}{d\epsilon}$$

Substitution into the above expressions yields

$$r_1 = -\frac{dH}{d\epsilon} - \frac{2dH_2}{d\epsilon} + \frac{dO_2}{d\epsilon}$$

$$r_8 = \frac{d(-H_2O - H - 2H_2 + O_2)}{d\epsilon} = \frac{dN}{d\epsilon}$$

The choice between the two three-body reactions, ① and ②, to determine the rate-controlling step to be used in the Bray analysis is somewhat more difficult. One approach is the substitution of actual concentrations of the participating species in the equation $r_k = k_f AB\rho^2$ for bimolecular reactions

or $r_k = k_f = AB\rho^3/M$.   The density is determined from the gas law,

$$\rho = \frac{PM}{RT}$$

where

      ρ = density, $g\,cc^{-1}$

      P = pressure, atm

      M = average gas molecular weight, $g\,mole^{-1}$

      T = temperature, °K

      R = gas constant, 82.057 atm cc $deg^{-1}\,mole^{-1}$

The evaluation of r_k for the throat conditions yielded a value for reaction ② of 1.4×10^{-2}, while r_k for reaction ① was 2.8×10^{-3}.   Reaction ① appears to be rate controlling by this criterion, but since the concentration influences the final result, a concentration of little importance to the total chemical process could be construed to control the entire process. For this reason the changes in H_2 and H_2O concentration in a equilibrium process might be considered.   At a mixture ratio of 4.5 the $\Delta H_2O = 0.069$ and the $\Delta H_2 = 0.013$ moles/100 g between the chamber and the throat.   This relative difference continues beyond the throat; therefore, a change in the H_2O formation would influence the performance more than a change in H_2 formation.   The enthalpy changes in the two reactions are almost equal.   As a first approximation $H + OH \rightarrow H_2O$ looks like a rate-controlling step.

In fact, $H + H + M \rightarrow H_2 + M$ might be the rate-controlling step.   Since the two reactions have similar rates, two freeze points could be determined, using each of the rate-controlling steps separately.

Evaluation of the freeze point for the same nozzle for a hydrogen-oxygen propellant at a mixture ratio of 4.5 and chamber pressure, P_c, of 100 gave only slightly different freeze points by varying the rate-controlling step.   For the $H + H + M \rightarrow H_2 + M$ step the freeze point occurred at an area

ratio of 1.26, representing a 1.3 per cent loss in vacuum specific impulse at an area ratio, ϵ, of 50. When $H + OH + M \rightarrow H_2O + M$ was considered as the rate-controlling step, the freeze point was at an area ratio of 1.58, which gave an impulse 2.5 sec higher than the area ratio of freezing, ϵ_f, of 1.26. The temperatures at the freeze points were 2568 and 2424°K, respectively.

The kinetics developed in the following section for N_2O_4-aerozine were also applied to the same H_2-O_2 propellant and yielded a freeze point of 1.39, an intermediate value between the two points found using the kinetics developed in this section. For H_2-O_2 the variations in the selected kinetics produced only small changes in the freeze point. Since the smallest value, 1.26, represents the largest impulse loss, it is the most conservative estimate of the freeze point.

IV. N_2O_4-AEROZINE SYSTEMS

The composition of an N_2O_4-aerozine propellant at a mixture ratio of 2 is shown in Table 4. The analysis which follows is valid for mixture ratios between 1.6 and 2.3.

Table 4. N_2O_4-Aerozine Systems, $P_c = 100$ lb in^{-2}

Composition, Moles/100 g	MR = 2.0	
	Chamber	Throat
H	0.0935	0.07376
O	0.03898	0.02866
OH	0.20515	0.16779
H_2O	1.70138	1.7615
H_2	0.29036	0.25881
CO	0.29099	0.26668
CO_2	0.23034	0.25466
NO	0.0504	0.03929
N_2	1.49253	1.49810
O_2	0.09179	0.07897

The kinetic steps given for the H_2-O_2 system apply, and in addition the reaction $CO + OH \rightarrow CO_2 + H$ should be considered. The k for this reaction is $\exp(-10^4 \text{ cal}/RT)$ cc mole^{-1} sec^{-1} and the $\Delta H_{298} = -24.88$ kcal. The reaction is fast compared to the three-body reactions and couples with the $H_2O + H \rightarrow H_2 + OH$ reaction, giving the water gas reaction with a net ΔH_{298} of -9.8 kcal. The total energy gain is small. Nitrogen interacts with the oxygen and hydrogen species to such a small extent that it is considered inert. The only remaining species to include are the hydrogen-oxygen combinations which are the same as the products in the hydrogen-oxygen case.

The greatest difference between the combustion products of the two propellants is the change in H_2 concentration. For H_2-O_2, H_2 increases down the nozzle, while it decreases from the chamber to an ϵ of 8 for N_2O_4-aerozine. Since this is the area where freezing is expected to occur, the $H + H + M \rightarrow H_2 + M$ reaction no longer applies. This leaves $H + OH + M \rightarrow H_2O + M$ as the rate-controlling step; therefore, only one freeze point needs to be considered. The final set of equations chosen for the analysis were

① $H + OH + M \rightarrow H_2O + M$

② $O_2 + H + OH + O$

③ $O + H_2O + 2\,OH$

④ $H_2 + OH + H + H_2O$
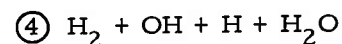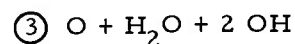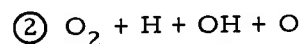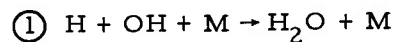
The expression of the rates as concentration changes results in the following relationships:

$$r_1 = \frac{dH_2O}{d\epsilon} + r_3 - r_4$$

$$r_3 = -\frac{dO}{d\epsilon} + r_2$$

$$r_4 = -\frac{dH_2}{d\epsilon}$$

$$r_2 = -\frac{dO_2}{d\epsilon}$$

Substitution into the above expressions yields

$$r_3 = -\frac{dO}{d\epsilon} - \frac{dO_2}{d\epsilon}$$

$$r_1 = \frac{d(H_2O - O - O_2 + H_2)}{d\epsilon} = \frac{dN}{d\epsilon}$$

A Bray analysis was calculated with these kinetics to determine the freeze points for four mixture ratios. Table 5 shows the freeze points, kinetic impulses, and performance losses (per cent) when compared to equilibrium impulses. The same results are shown graphically in Fig. 1.

Table 5. H_2O_4-Aerozine Freeze Points
and Performance Losses

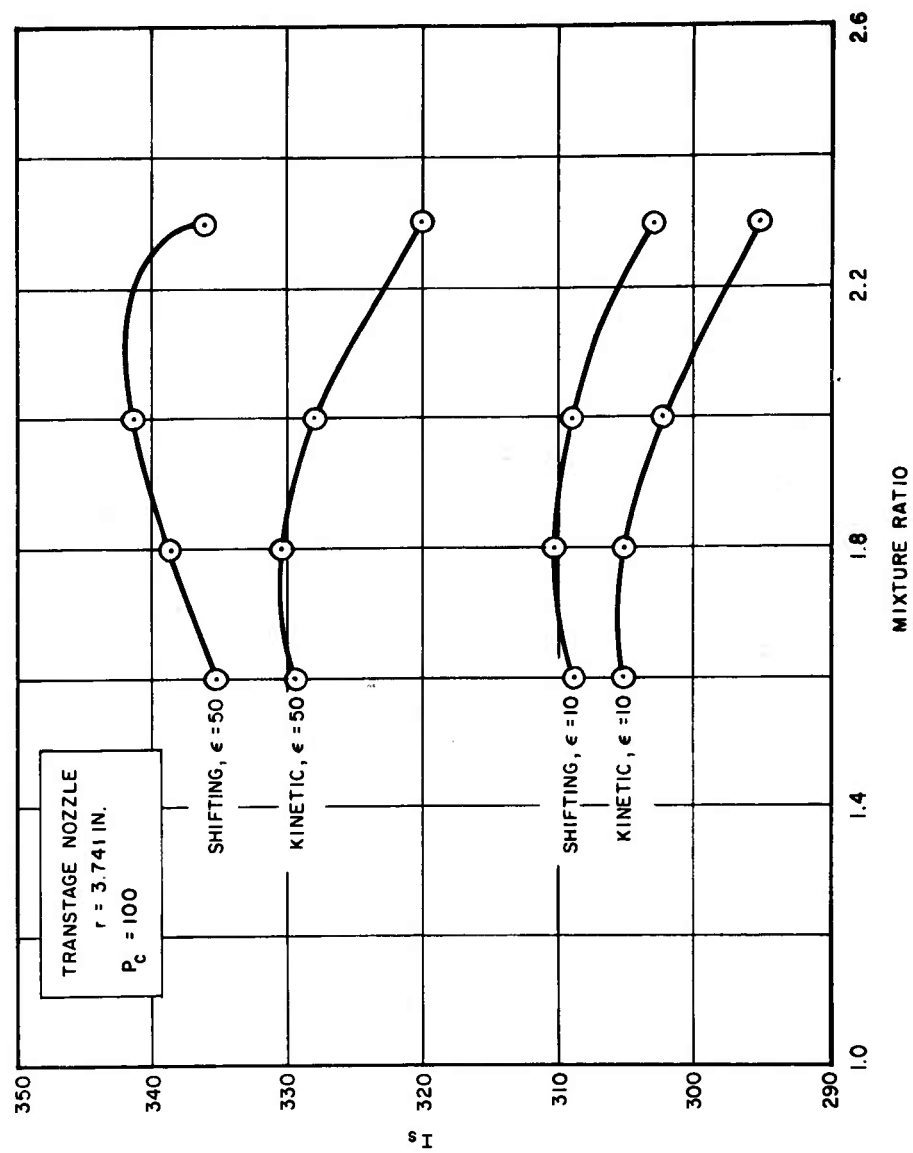| RC Step	P_c	MR	ϵ_f, Trans Nozzle	T_f, °K	I_s(vac) $\epsilon = 10$	Loss from equil, %	I_s(vac) $\epsilon = 50$	Loss from equil, %
H + OH + M → H_2O + M	100	1.6	1.28	2627	305.2	1.2	329.5	1.7
		1.8	1.43	2674	305.1	1.6	330.4	2.4
		2.0	1.48	2701	302.3	2.2	327.8	4.0
		2.3	1.40	2711	295.1	2.5	319.9	4.8

Fig. 1. N_2O_4-Aerozine, Kinetic and Equilibrium Specific Impulse

V. HYDROGEN-FLUORINE SYSTEMS

The products formed from a hydrogen-fluorine propellant are H_2, HF, H, and F. The product F_2 is present only at extremely high mixture ratios and then in small concentrations which are unimportant for Bray analysis. The reactions, their rate constants, and ΔH's selected for consideration are as follows:

Reactions	Rate Constants[a]	ΔH_{298}(kcal mole^{-1})
① $H + H + M \rightarrow H_2 + M$ $\quad\quad M = HF$	$k_1 = 1 \times 10^{19} T^{-0.5}$	-104
② $H + F + M \rightarrow HF + M$ $\quad\quad M = HF$	$k_2 = 1 \times 10^{19} T^{-0.5}$	-135
③ $F + H_2 \rightarrow HF + H$	$k_3 = 5 \times 10^{12} e^{\dfrac{-5.7 \times 10^3 \, cal}{RT}}$	-31
[a] The rates are based on those given in Ref. 5.		

The reaction $H_2 + F_2 \rightarrow 2\,HF$ is not considered a likely reaction kinetically. The product HF is formed by one of the above mechanisms.

The three-body reactions, ① and ②, represent the possible rate-controlling steps, since ③ is a faster bimolecular reaction releasing less energy and is more nearly in equilibrium than ① or ②.

The product HF was chosen as the third body since it is present in larger quantities than any other gas and is the largest contributor to the average molecular weight, which was used in the actual calculations as the third-body concentration.

A point to consider in choosing the rate-controlling step is whether or not it represents the chemical phenomena occurring in the nozzle. For a hydrogen-fluorine propellant at a chamber pressure of 150 psi and a mixture ratio of 12, there are 1.27 moles H, 0.17 moles F, 4.68 moles HF, and 0.84 moles H_2 in 100 grams for the throat conditions of a shifting equilibrium calculation. Since chamber pressure changes composition very little, the analysis which follows is applicable to the other pressures considered.

At a mixture ratio of 12 or 18 the $H + F + M \rightarrow HF + M$ is the predominant reaction. Upon substitution of the concentrations of the combustion products in an equilibrium calculation, the HF reaction is slower than the H_2 recombination and therefore was chosen as the rate-controlling step.

Choosing two independent rate equations and expressing them in terms of the species H_2 and HF, leads us to the following equations:

$$r_2 = \frac{d(HF)}{d\epsilon} - r_3 \qquad \text{and} \qquad r_3 = - \frac{d(H_2)}{d\epsilon}$$

Upon substitution

$$r_2 = \frac{d(HF)}{d\epsilon} \times \frac{d(H_2)}{d\epsilon} = \frac{d(HF + H_2)}{d\epsilon}$$

This final expression of r_2 is used for the nozzle recombination $dN/d\epsilon$.

This particular set of equations is valid for mixture ratios which yield a large amount of F and H which may recombine into HF and H_2. However for lower mixture ratios, 4 to 8, which are deficient in free fluorine, it is a dubious treatment. The chemical process occurring is primarily the recombination of hydrogen which is expressed by k_1 and should be used as the rate-controlling step.

For comparative purposes the freeze point was determined for mixture ratios 5.2 and 8.0, using k_1 and k_2 separately as the rate-controlling steps. The freeze points and corresponding specific impulses are shown in Table 6.

At a mixture ratio of 8, for example, the use of rates k_1 and k_2 yields freeze points of 1.50 and 3.85 for the transtage nozzle, respectively, corresponding to I_s losses of 2.0 and 0.5 per cent at an area ratio of 50. The absolute difference in specific impulse is 8 sec. The rate-controlling step selected can influence the freeze point significantly and therefore should be selected carefully. In general, the larger the freezing area ratio, the smaller the performance loss.

Since the rate of the $H + F + M \rightarrow HF + M$ was estimated, the effect of a different value was investigated. The constant was decreased one decade to $1 \times 10^{18} T^{-0.5}$. At a mixture rate of 12 the freeze point dropped from 2.99 to 1.79, using the new rate. The performance varied by 7.6 sec at an area ratio of 10. Similar losses occurred for the other mixture ratios and are noted in the tabulation. Until the reaction rate constants are determined experimentally it is difficult to find an exact freeze point from the Bray method. Various alternatives must be considered to obtain minimum and maximum values.

A comparison of performance losses due to kinetic processes for different chamber pressures shows that the losses are greater at the lower pressures since freezing occurs at smaller area ratios. For a H_2-F_2 propellant at a mixture ratio of 12 and ϵ of 10 there is only 0.95 per cent performance loss for a transtage nozzle at a pressure of 300 while the loss is 2.7 per cent at 100 psi.

The kinetic freeze point occurs at higher area ratios for higher mixture ratios for the H_2-F_2 series (Fig. 2). This seems logical since the total number of uncombined H and F atoms in the chamber increases with mixture ratio. At a mixture ratio of 5.2 there are 0.48 moles of atoms and at 18 there are 1.78 moles. Essentially, the HF and H_2 recombination processes are already more complete in the chamber at low mixture ratios;
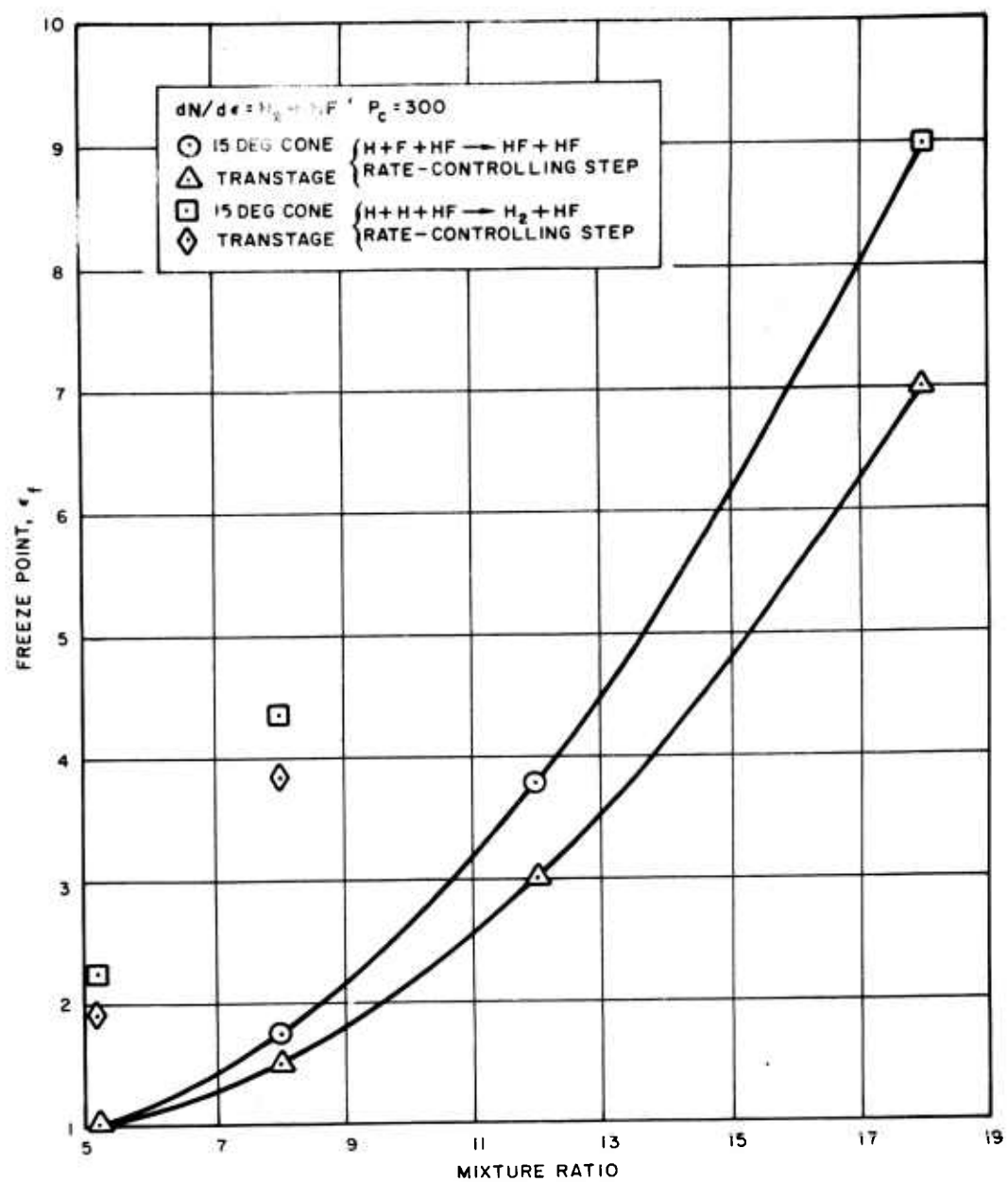
-21-

Fig. 2. Hydrogen-Fluorine Freeze Points

therefore, the freeze point occurs nearer the chamber. This does not prove that performance losses are the least at low mixture ratios, since the freeze point moves downstream and allows the energy producing reactions to occur at the higher mixture ratios. Specific impulses and performance losses are shown in Table 6 and Fig. 3.

Since a complete Bray analysis for a series of propellants is a tedious calculation, we attempted to find a simpler, empirical correlation. Assuming the same rate-controlling step for each mixture ratio, we found that the temperature at each freeze point was similar. Although the chamber temperature for mixture ratios 5.2 through 18.0 varied by 1400 deg, the freezing temperatures for a given nozzle varied only 300 deg. In Fig. 4 the temperature versus area ratio for each mixture ratio is plotted, and the freeze point is noted for each of two nozzles. The freeze points for mixture ratios 5.2 and 8.0 are those which occur when the hydrogen recombination step is considered the rate-controlling step. The temperature at the freeze points obtained from different rate-controlling processes does not fall within the same range. The various kinetic processes used in the analysis not only produce quite different freeze points but also widely varied temperatures.

As a first approximation, the freeze point for a chemical system governed by the same kinetic process as in a previously analyzed system, should fall within the same temperature range.

Another empirical correlation was attempted by comparing the percentage of atoms in the chamber which were recombined at the freeze point, determined from $H + F + M \rightarrow HF + M$ reaction, for the various mixture ratios. Figure 5 shows the results: the degree of recombination decreases for higher mixture ratios or decreases for the more highly dissociated systems.

Table 6. Hydrogen-Fluorine Freeze Points and Performance Losses

| RC Step	P_c	MR	ϵ_f	T_f, °K	I_s(vac) $\epsilon = 10$	Equilibrium Loss, %	I_s(vac) $\epsilon = 50$	Equilibrium Loss, %
H + F + M → HF + M M = HF	300	5.2	1.0(Cone) 1.0(Trans.)	2930 2930	434.3 434.3	1.9 1.9	459.03 459.03	2.3 2.3
H + F + M → HF + M M = HF	300	8.0	1.5(Trans.) 1.75(Cone)	3042 2930	436.8 439.0	1.9 1.4	463.09 467.3	3.1 2.2
H + F + M → HF + M M = HF	300	12.0	2.99(Trans.) 3.79(Cone)	3106 2973	435.9 437.6	0.95 0.56	467.0 470.1	2.6 1.9
H + F + M → HF + M M = HF	300	18.0	7.0(Trans.) 9.0(Cone)	3209 3100	428.7 429.1	0.12 0.02	466.4 468.7	1.6 1.2
H + F + M → HF + M M = HF	100	12.0	1.76(Trans.) 2.39(Cone)	3310 2886	423.2 427.7	2.7 1.7	450.2 456.8	5.5 4.1
H + H + M → H_2 + M M = HF	300	5.2	1.92(Trans.) 2.25(Cone)	2174 2046	442.1 442.4	0.11 0.05	468.9 469.25	0.17 0.08
		8.0	3.85(Trans.) 4.35(Cone)	2400 2318	444.2 444.7	0.23 0.11	475.60 476.1	0.52 0.32
H + F + M → HF + M $k = 1 \times 10^{18} T^{-0.5}$	300	8.0	1.1(Trans.)	3318	430.0	3.4	455.4	4.7
		12.0	1.79(Trans.)	3419	430.0	2.3	457.9	4.5
		18.0	3.65(Trans.)	3496	425.1	0.96	457.6	3.5
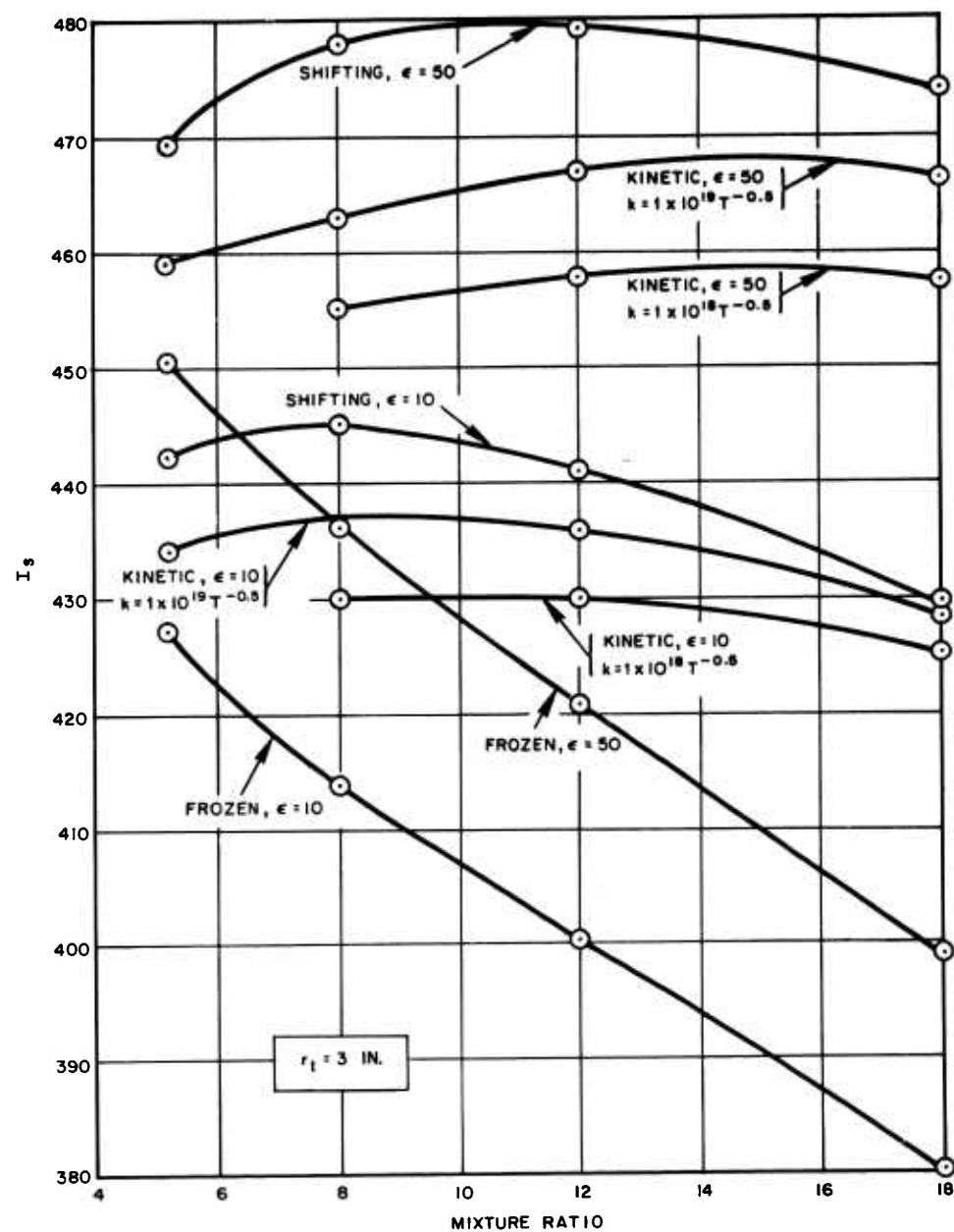
Fig. 3.   Hydrogen-Fluorine, Kinetic and Equilibrium
Specific Impulse
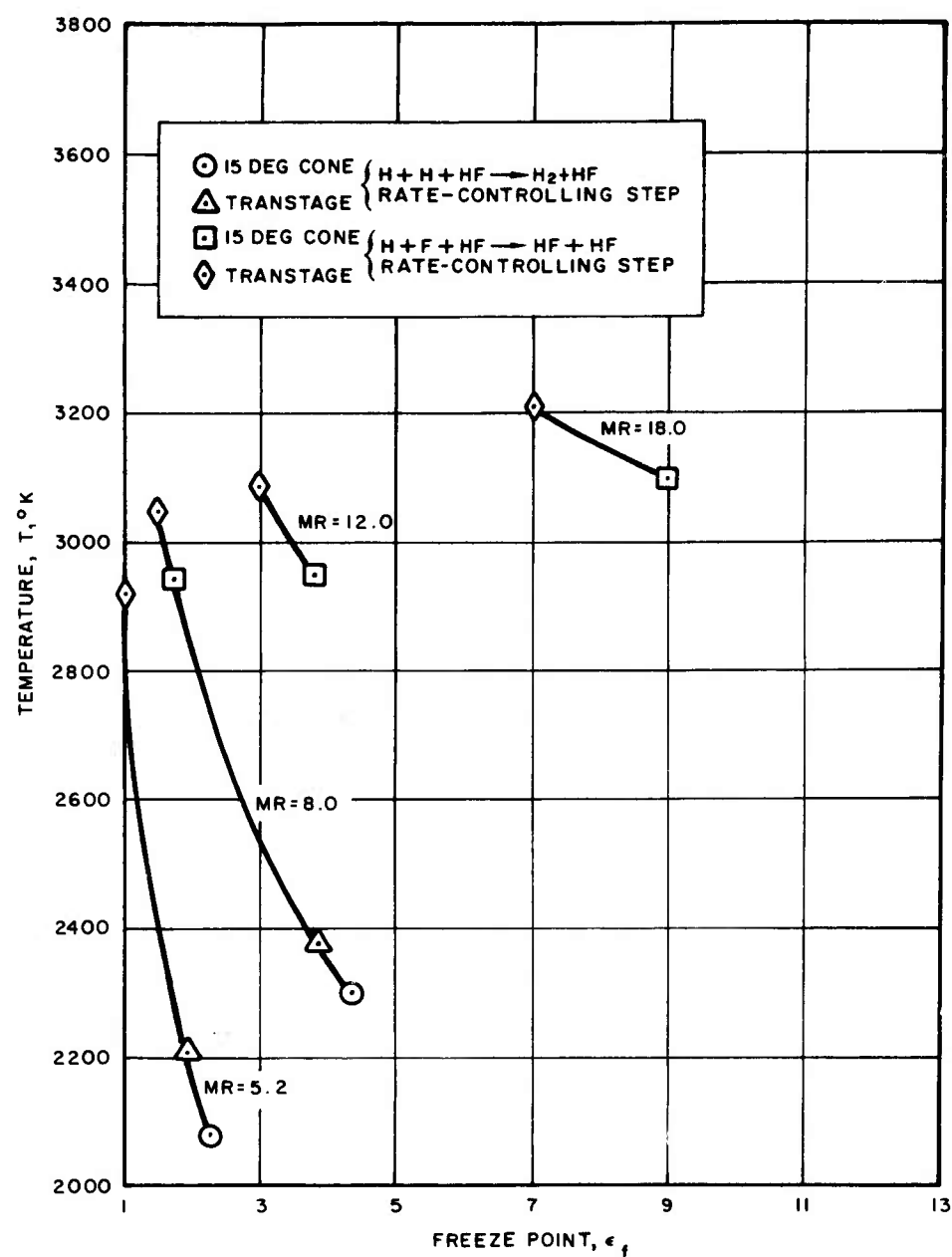
Fig. 4. Temperature at Freeze Point for
Hydrogen-Fluorine

70

60 ⊙

50

40 ⊙

RECOMBINATION AT FREEZE POINT, ϵ_ℓ, PERCENT

⊙

30

⊙

20

10

0
5   10   15   20

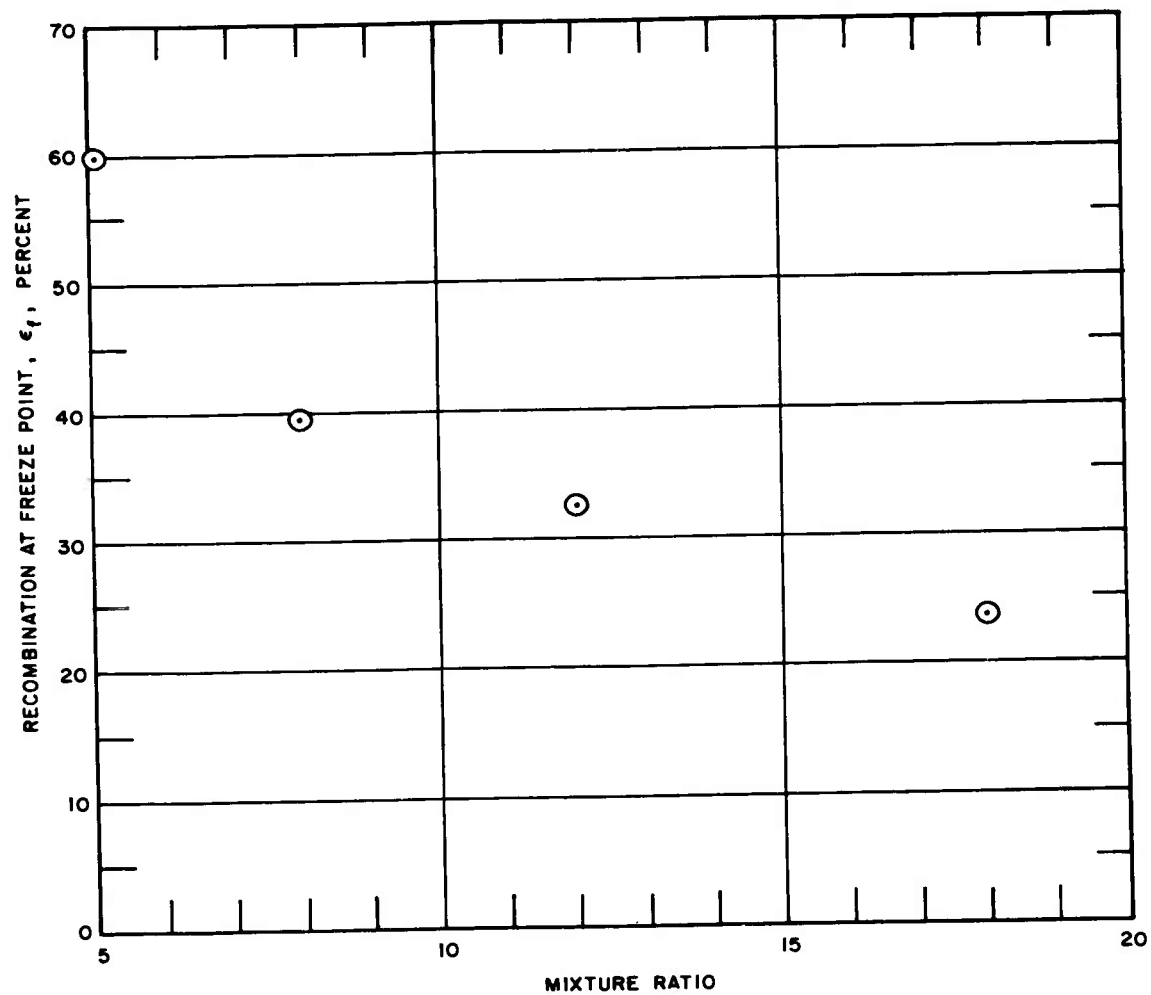MIXTURE RATIO

Fig. 5. Recombination at Freeze Point for
Hydrogen-Fluorine, Per Cent

VI. HYDROGEN-CHLORINE SYSTEMS

In order to compare the freeze point as determined by the Bray analysis for propellants containing different halogens, an arbitrary H_2-Cl_2 propellant was selected. The equilibrium performance was calculated for a mixture ratio, 22, which contained the same mole ratio of Cl_2 to H_2 as an H_2-F_2 propellant at a mixture ratio of 12.

The chlorine propellant contained only 0.00723 moles of atoms in the chamber and 0.00148 moles at the throat which would be available for a recombination process. The comparable fluorine propellant contained 1.80 moles of atoms in the chamber. For all practical purposes, an inspection of composition showed that the chlorine propellant selected was frozen in the chamber.

Of course, other chlorine-containing propellants, such as a solid propellant with NH_4ClO_4, could have been selected, but the products of combustion would be too numerous for a simple Bray approach as we were applying. The following reaction rates were selected or estimated to attempt a Bray analysis.

Reaction	Rate Constants	ΔH_{298} (kcal mole^{-1})
① $H + H + M \rightarrow H_2 + M$	$k_1 = 1 \times 10^{19} T^{-0.5}$	-104.2
② $H + HCl \rightarrow H_2 + Cl$	$k_2 = 1.45 \times 10^{11} T^{-0.5} \frac{-4000 \text{ cal}}{RT}$	-1.21
③ $H_2 + Cl \rightarrow HCl + H$	$k_3 = 2.82 \times 10^{11} T^{-0.5} \frac{-5000 \text{ cal}}{RT}$	+1.21
④ $H + Cl + M \rightarrow HCl + M$	$k_4 = 1 \times 10^{19} T^{-0.5}$	-103.0

Reactions ② and ③ were obtained from Benson (Ref. 5). Reactions ① and ④ were estimated from the fluorine data, assuming that HCl as the third body would affect the reaction in the same way as HF, and that the H + Cl recombination is the same as the H + F recombination.

It was found, as had been anticipated, that freezing occurred before the throat when the Bray technique was applied.

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DOCUMENT CONTROL DATA - R&D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)	2a. REPORT SECURITY CLASSIFICATION
Aerospace Corporation El Segundo, California	Unclassified
	2b. GROUP

3. REPORT TITLE

NONEQUILIBRIUM ROCKET NOZZLE RECOMBINATION LOSSES

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

5. AUTHOR(S) (Last name, first name, initial)

Cook, E. A. and Schieler, L.

6. REPORT DATE	7a. TOTAL NO. OF PAGES	7b. NO. OF REFS
15 October 1964	37	6

8a. CONTRACT OR GRANT NO.	9a. ORIGINATOR'S REPORT NUMBER(S)
AF 04(695)-469	TDR-469(9210-02)-1
b. PROJECT NO.	
c.	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)
d.	SSD-TDR-64-183

10. AVAILABILITY/LIMITATION NOTICES

Qualified requesters may obtain copies of this report from DDC.

11. SUPPLEMENTARY NOTES	12. SPONSORING MILITARY ACTIVITY
	Space Systems Division Air Force Systems Command Los Angeles, California

13. ABSTRACT

Nonequilibrium performance losses are interpreted in terms of radical concentrations and extent of recombination throughout the expansion process. A brief description of the Bray method for determining the location of departure from equilibrium flow in a rocket nozzle is given. The analysis is applied to N_2O_4-aerozine, H_2-O_2 and H_2-F_2 propellants and a hypothetical H_2-Cl_2 system to obtain the point of effective freezing as a function of area ratio. The kinetic rates for the reactions occurring in the combustion process are discussed, and the values for the rates are included.

DD FORM 1473
(FACSIMILE)

14.	KEY WORDS

Rocket Performance Losses

Nonequilibrium in Rocket Nozzles

Bray Analysis

Chemical Reaction Rates

Recombination of Radicals

Propellant Combustion Products

Abstract (Continued)